The Canadian Mineralogist
Vol. 36, pp. 1039-1043 (1998)

THE CRYSTAL STRUCTURE OF $Na_2MgGd_2(Si_4O_{12})F_2$ AND ITS RELATIONSHIP WITH LEUCOPHANITE

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ABSTRACT

The structure of a newly synthesized rare-earth fluorosilicate, $Na_2MgGd_2(Si_4O_{12})F_2$, was determined using single-crystal X-ray diffraction. It crystallizes in the monoclinic system, $P2_1/c$, with unit-cell parameters *a* 5.178(3), *b* 7.510(2), *c* 14.381(4) Å, β 90.22(2)°, *V* 559.1(2) $Å^3$ and Z = 2. The structure consists of SiO_4 tetrahedra in [010] zigzag chains connected by MgO_4F_2 octahedra. The stacking of the resulting $Mg(Si_4O_{12})F_2$ sheets defines voids in which Gd^{3+} and Na^+ are found. Similar silicate chains, connected by BeO_3F tetrahedra, exist in leucophanite and result in $Be_2(Si_4O_{12})F_2$ sheets.

Keywords: fluoride, silicate, rare earth, new synthetic species, structure.

SOMMAIRE

Nous avons détérminé la structure d'un nouveau fluorosilicate de terre rare synthétique, $Na_2MgGd_2(Si_4O_{12})F_2$ par diffraction X sur monocristal. La maille est monoclinique, *a* 5.178(3), *b* 7.510(2), *c* 14.381(4) Å, β 90.22(2)°, *V* 559.1(2) $Å^3$, $P2_1/c$ avec Z = 2 . La structure contient des chaînes de tetraèdres SiO_4 en zigzag selon [010], connectées par des octaèdres MgO_4F_2. Les feuillets $MgSi_4O_{12}F_2$ qui en résultent définissent des espaces où s'insèrent Gd^{3+} and Na^+. On rencontre des chaînes silicatées similaires, connectées par des tétraèdres BeO_3F, dans la leucophanite; il s'agit dans ce cas de feuillets $Be_2(Si_4O_{12})F_2$.

Mots-clés: fluorure, silicate, terre rare, nouvelle espèce synthétique, structure.

INTRODUCTION

Few structural families of fluorosilicates exist; the best known belong to the apatite and epidote groups. These compounds are mainly found in the Earth's crust. However, it was recently shown that the fluoride ion can substitute for hydroxyl ions in hydrous $[Mg_{12}Si_4O_{19}(OH)_2]$ or superhydrous $[Mg_{10}Si_3O_{14}(OH)_4]$ phases B. Consequently, fluorine could well play a role in the behavior of the upper mantle and transition zone (Hazen *et al.* 1997).

We present here information on a new fluorosilicate, $Na_2MgGd_2(Si_4O_{12})F_2$, which shows interesting analogies with leucophanite $NaCaBe(Si_2O_6)F$ (Cannillo *et al.* 1967, 1969, 1992, Grice & Hawthorne 1989) and the synthetic compound $Ca_3Mn_2(Si_4O_{12})O_2$ (Moore & Araki 1979). This work forms part of general study of mixed-anion phases of rare-earth elements, including fluoroborates, fluorocarbonates and fluorosilicates. The stability of these fluoride compounds in terms of P and T is investigated in connection with conditions of mineral formation. Grice & Chao (1997a) have recently proved the existence of a structural similarity between synthetic and mineral fluorocarbonates; a synthetic fluorocarbonate, $Na_3La_2(CO_3)_4F$ (Mercier *et al.* 1993) is isostructural with lukechangite (Grice & Chao 1997b).

EXPERIMENTAL DETAILS

$Na_2MgGd_2(Si_4O_{12})F_2$ was prepared by hydrothermal synthesis. A mixture of GdF_3, Na_2CO_3, and $(MgO)_2(SiO_2)_3•5H_2O$ in molar proportion 2:3:2 was inserted in a platinum tube. After sealing, the tube was submitted to an external pressure of nitrogen (85 MPa) in an autoclave and then heated at 700°C during 36 hours at P_{max} = 190 MPa. Chemical analysis of several small crystals by energy-dispersion spectroscopy with a scanning electron microscope (Hitachi S2300) led us to detect all the elements of the new compound. The presence of an impurity, $NaMgF_3$, was confirmed by an X-ray powder-diffraction pattern of the bulk sample.

X-ray-diffraction data were collected up to $2\theta = 70°$ from a single crystal of $Na_2MgGd_2(Si_4O_{12})F_2$ selected following an optical examination, and studied at room temperature on a Siemens AED2 four-circle diffractometer. The unit cell was obtained from a long-exposure

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TABLE 1. $Na_2MgGd_2(Si_4O_{12})F_2$: CHARACTERIZATION AND INFORMATION ON DATA COLLECTION

Space group	$P2_1/c$	Crystal size (μm)	114 x 92 x 40
a (Å)	5.178(3)	Radiation	MoKα
b (Å)	7.510(2)	Absorption (cm^{-1})	124.4
c (Å)	14.381(4)	Measured reflections	5254
β (°)	90.22(2)	Reflections used ($I > 2\sigma(I)$)	1943
V ($Å^3$)	559.1(2)	Refined parameters	107
Z	2	Final R/R_w (%)	3.93/9.87
$d_{calc.}$ (g/cm^3)	4.318	Secondary extinction	$1.5(6)10^{-6}$

TABLE 3. $Na_2MgGd_2(Si_4O_{12})F_2$: INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Si1 - O2	1.594(4)	Gd - O5	2.275(4)	O1 - Si1 - O2	112.5(2)
- O4	1.603(4)	- O6	2.288(4)	- O3	104.5(2)
- O1	1.644(4)	- O2	2.316(4)	- O4	108.6(2)
- O3	1.678(4)	- O4	2.348(4)	O2 - Si1 - O4	116.6(2)
<Si1- O>	1.630(4)	- O6	2.392(4)	- O3	111.3(2)
		- F1	2.471(4)	O3 - Si1 - O4	102.2(2)
Si2 - O5	1.611(4)	- F1	2.473(3)		
- O6	1.613(4)	- O3	2.866(4)	O1 - Si2 - O3	104.9(2)
- O1	1.650(4)			- O5	111.4(2)
- O3	1.662(4)	Na - F1	2.316(4)	- O6	106.9(2)
<Si2- O>	1.634(4)	- O2	2.371(5)	O3 - Si1 - O5	110.0(2)
		- O1	2.537(5)	- O6	110.4(2)
Mg - F1	1.971(4) x 2	- O4	2.551(5)	O5 - Si1 - O6	112.9(2)
- O4	2.086(4) x 2	- O2	2.551(5)		
- O5	2.089(4) x 2	- O3	2.730(5)		
		- O1	2.956(5)		

rotation photograph. The intensities of 5254 reflections were recorded. After corrections for Lorentz and polarization factors and absorption (Sheldrick 1976), a set of 1943 independent reflections with $I > 2\sigma(I)$ was extracted. Structure refinements were carried out by using SHELXS–86 and SHELXL–93 programs (Sheldrick 1986, 1993). In Table 1, we present the crystallographic data and information about data collection.

STRUCTURE DETERMINATION AND DESCRIPTION

The conditions of systematically absent reflections led to the centrosymmetric space-group $P2_1/c$ (14). The position of the gadolinium atoms was first disclosed by a Patterson map. The positions of the other elements were revealed by successive refinements and difference Fourier maps. Finally, the refinement of the anisotropic atomic displacement parameters U_{ij} and secondary extinction factor brought the R factor down to 0.0393 ($R_w = 0.0987$). The final residual electron-densities were –5.75 and 5.63 e–/$Å^3$ at 0.63 Å from the gadolinium site. The final atomic coordinates with equivalent isotropic atomic displacement parameters, main interatomic distances and angles are reported in Table 2 and 3, respectively. According to the model of Brese & O'Keeffe (1991), an analysis of bond valences demonstrates a result consistent with the formula $Na_2MgGd_2(Si_4O_{12})F_2$ (Table 4). Anisotropic atomic displacement parameters and observed and calculated structure-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council Of Canada, Ottawa, Ontario, Canada K1A 0S2.

TABLE 2. $Na_2MgGd_2(Si_4O_{12})F_2$: ATOMIC COORDINATES, SITE DESIGNATION, AND ISOTROPIC EQUIVALENT DISPLACEMENT PARAMETERS

Atom	Site	x	y	z	B_{eq}* [$Å^2$]
Gd	4e	0.51375(5)	0.22882(3)	0.95706(2)	0.427(7)
Si1	4e	0.0231(3)	0.2407(2)	0.8140(1)	0.43(2)
Si2	4e	0.0370(3)	0.3718(2)	0.6149(1)	0.42(2)
Mg	2c	0	0	1/2	0.49(3)
Na	4e	0.5040(6)	0.4570(5)	0.2106(2)	1.89(5)
F	4e	0.3366(7)	0.4607(5)	0.0610(2)	0.70(4)
O1	4e	0.1443(8)	0.2726(6)	0.7098(3)	0.70(5)
O2	4e	0.7152(8)	0.2423(5)	0.8137(3)	0.70(5)
O3	4e	0.1390(8)	0.0418(5)	0.8471(3)	0.62(5)
O4	4e	0.1636(8)	0.3733(6)	0.8853(3)	0.60(5)
O5	4e	0.8602(8)	0.2398(5)	0.5535(3)	0.67(5)
O6	4e	0.2868(8)	0.4433(5)	0.5595(3)	0.68(5)

* Isotropic equivalent displacement parameters defined as : $B_{eq} = \left(\frac{8\pi^2}{3}\right)\sum_i \sum_j U_{ij} |\vec{a}_i^*| |\vec{a}_j^*| \vec{a}_i \vec{a}_j$

The crystal structure of $Na_2MgGd_2(Si_4O_{12})F_2$ can be described in terms of chains of vertex-sharing SiO_4 tetrahedra (Fig. 1a). These Si_4O_{12} zigzag chains, along [010], are connected by sharing oxygen atoms at the corners of MgO_4F_2 octahedra in order to build $MgSi_4O_{12}F_2$ slabs parallel to (100) at $x \approx 0$ (Fig. 1a). The succession of these slabs, along [100], defines voids in which Gd^{3+} and Na^+ ions are inserted. The edge-shar-

TABLE 4. $Na_2MgGd_2(Si_4O_{12})F_2$: BOND-VALENCE CALCULATIONS

	Gd1	**Si1**	**Si2**	**Mg**	**Na**	**Σs**
F	0.24^{x2}			0.35^{x2}	0.18	1.01
O1		0.95	0.93		0.14/0.04	2.02
O2	0.51	1.08			0.21/0.13	1.93
O3	0.12	0.86	0.90		0.08	1.96
O4	0.46	1.06		0.35^{x2}	0.13	2.00
O5	0.57		1.04	0.34^{x2}		1.95
O6	0.55/0.41		1.03			1.99
Σs	3.10	3.95	3.90	2.08	0.91	

ing Gd and Na polyhedra form infinite [010] chains at $x \approx 1/2$, parallel to the orientation of the silicate chains (Fig. 2). According to the classification of Liebau (1985), $Na_2MgGd_2(Si_4O_{12})F_2$ is a single-chain silicate (monopolysilicate) with $\{uB, 1^1_\infty\}$ $[^4Si_4O_{12}]^{8-}$ chains. As expected, long Si–O bond distances are found in these chains, with O1 and O3 being the bridging oxygen atoms (Table 3). Sodium and gadolinium adopt 7-fold and 8-fold coordinations, respectively.

From the compilation of eight monopolysilicates given by Liebau (1985), only leucophanite and synthetic $Ca_3Mn_2(Si_4O_{12})O_2$ exhibit analogous infinite $[Si_4O_{12}]$ chains. For structural comparisons, we define the periodicity in the slab of silicate chains, $u_{//}$ and $u_{\perp}$, as the parameters parallel and perpendicular respectively to the silicate chain; u_L represents the interlayer spacing. In $Na_2MgGd_2(Si_4O_{12})F_2$, leucophanite and $Ca_3Mn_2(Si_4O_{12})O_2$, the cell parameters are respectively ($u_{//}$, $2u_{\perp}$, u_L), ($u_{//}$, $u_{\perp}$, $2u_L$) and ($u_{//}$, $2u_{\perp}$, $2u_L$) (Fig. 1). The values of $u_{//}$, $u_{\perp}$, u_L are similar and compared in Table 5. In $Na_2MgGd_2(Si_4O_{12})F_2$, consecutive chains are rotated and slightly shifted along [010] in order to accommodate the octahedral coordination of magnesium (Figs. 1a, 3). A similar arrangement was noted in $Ca_3Mn_2(Si_4O_{12})O_2$. Consequently, the periodicity is $2u_Z$. In leucophanite, the chains are not rotated, and their connection is provided by BeO_3F tetrahedra (Figs. 1b, 3); the periodicity is u_Z. The layer compositions are $Be_2(Si_4O_{12})F_2$ in leucophanite and $Mn(Si_4O_{12})O_2$ in $Ca_3Mn_2(Si_4O_{12})O_2$ (Figs. 1b, c). The number of interlayer cations, Na_2Gd_2, Na_2Ca_2 or Ca_3Mn, is identical in all phases. Owing to stacking of the interlayer cations, the cell parameter is $2u_L$ for leucophanite and $Ca_3Mn_2(Si_4O_{12})O_2$. Four SiO_4 tetrahedra and the binding polyhedron form a distorted pentagonal void (Figs. 1a, b, c). The parameter $u_{//}$ increases from leucophanite to $Ca_3Mn_2(Si_4O_{12})O_2$. This variation is related to the lengthening of the edge of the pentagon associated with the binding polyhedron (2.580 Å in BeO_3F, 2.821 Å in MnO_6 and 2.892 Å in MgO_4F_2). Similarly, the Si–O–Si angles ($\delta_{//}$) associated with the Si–Si orientation parallel to the chain axis increase (Fig. 1, Table 5). In addition, the Si–O–Si angles ($\delta_{\perp}$) corresponding to the Si–Si orientation perpendicular to the chain axis open from 126.3° in $Ca_3Mn_2(Si_4O_{12})O_2$ to 133.7° in $Na_2MgGd_2(Si_4O_{12})F_2$.

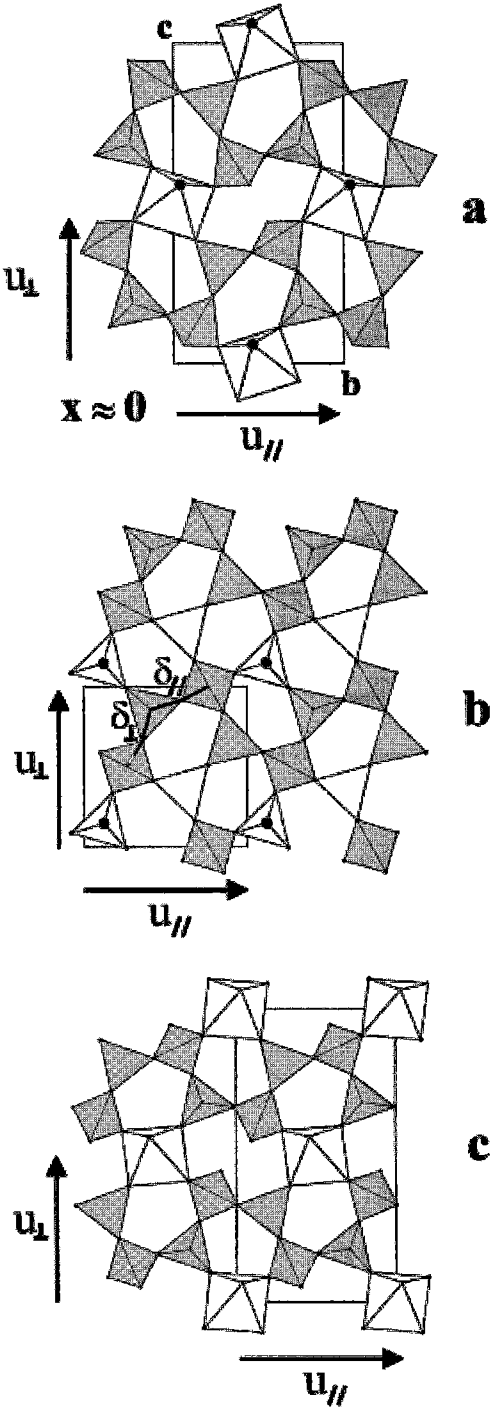

FIG. 1. Projections of a) $MgSi_4O_{12}F_2$, b) $Be_2(Si_4O_{12})F_2$ and c) $Mn(Si_4O_{12})O_2$ sheets in $Na_2MgGd_2(Si_4O_{12})F_2$, leucophanite and $Ca_3Mn_2(Si_4O_{12})O_2$, respectively. The large full circles give the fluorine positions ; the unit cell is also indicated.

TABLE 5. STRUCTURAL PARAMETERS OF $Na_2MgGd_2(Si_4O_{12})F_2$, LEUCOPHANITE AND $Ca_3Mn_2(Si_4O_{12})O_2$

	$Na_2MgGd_2(Si_4O_{12})F_2$	leucophanite	$Ca_3Mn_2(Si_4O_{12})O_2$
$u_{//}$ (Å)	7.510(2)	7.401(2)	7.62(1)
$u_\perp$ (Å)	7.190(2)	7.412(2)	7.13(2)
u_L (Å)	5.178(3)	4.995(1)	5.012(2)
$\delta_{//}$ (°)	125.5(2)	122.3(2)	125.3(1)
$\delta_\perp$ (°)	133.7(3)	123.2(2)	126.3(1)

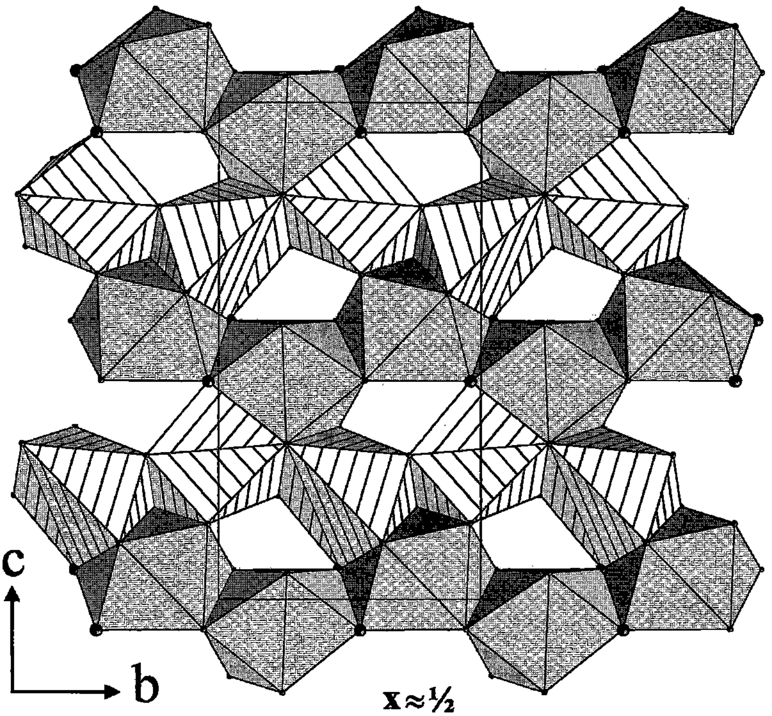

FIG. 2. Infinite chains defined by the arrangement of sodium (hatched) and gadolinium polyhedra in $Na_2MgGd_2(Si_4O_{12})F_2$.

As in leucophanite, the low isotropic displacement factors (B_{eq}) of $Na_2MgGd_2(Si_4O_{12})F_2$ for all elements except Na indicate a very stable structure (Table 2). Moreover, the main contribution of the high value of B_{eq} for Na^+ comes from U_{22} [0.025(1) and 0.029(2) in leucophanite and $Na_2MgGd_2(Si_4O_{12})F_2$, respectively]. The arrangement of the chains of Na^+ polyhedra along [010] is the same for both structures. These similar features suggest the existence of thermally activated Na^+ ionic conductivity.

The structural type of $Na_2MgGd_2(Si_4O_{12})F_2$ is currently studied for other rare-earth elements, and optical analyses are in progress. The substitution of Mg^{2+} by Fe^{2+} will be also tested, and the stability of the ferrous fluorosilicate will be investigated as a function of pressure and temperature. Additional temperature-dependent experiments, including diffraction and conductivity measurements, will be performed in order to test the mobility of sodium.

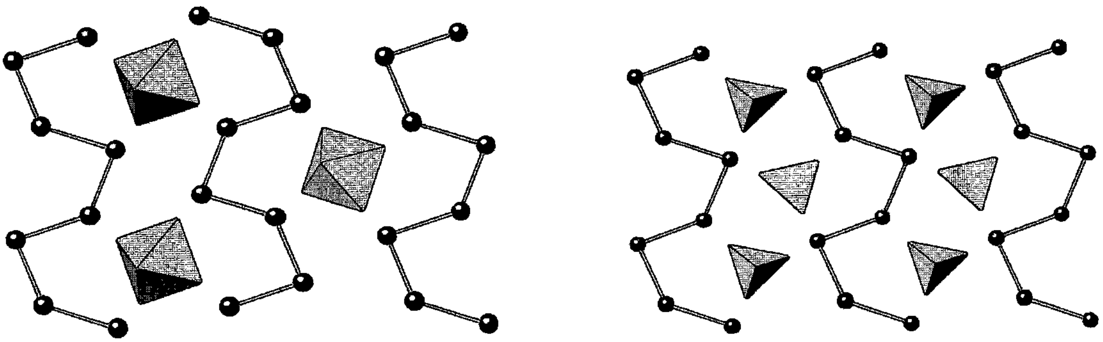

FIG. 3. Schematic representation of $MgSi_4O_{12}F_2$ (left) and $Be_2(Si_4O_{12})F_2$ slabs (right) in $Na_2MgGd_2(Si_4O_{12})F_2$ and in leucophanite, respectively (only silicon atoms of SiO_4 tetrahedra are indicated together with BeO_3F tetrahedra and MgO_4F_2 octahedra).

ACKNOWLEDGEMENTS

We thank Drs. Elio Cannillo and Joel D. Grice for their helpful reviews.

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Received April 7, 1998, revised manuscript accepted June 24, 1998.